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ERRORS IN THE DETERMINATION OF SILICA

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ERRORS IN THE DETERMINATION OF SILICA

BY

SHERMAN RAY WILSON

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Introduction

In the analysis of a silicate it is a well established practice to correct for impurities which contaminate the silica by evaporating with sulfuric and hydrofluoric acids, when a weighable residue always results. It is the purpose of this investigation to determine some of the factors which influence the amount and composition of this residue, to observe the effect upon the percentage of silica obtained, and to study especially the effect of lime on the determination of silica.

An outline of the method commonly employed in the analysis of silicates is as follows:

1. About .5 gm. of the rock powder is fused with from four to six parts of sodium carbonate.
2. The fused mass is dissolved in about 100 cc. of dilute hydrochloric acid. (1 - 4)
3. The solution is evaporated to dryness on a steam bath.
4. The dry mass is drenched with about 10 cc. of concentrated hydrochloric acid (S.G. 1.2) and again evaporated to dryness. This process is repeated three times and the substance finally heated for an

hour in an air bath at 110 degrees.

5. The dehydrated mass is next drenched with 10-15 cc. of concentrated hydrochloric acid. After a short time water is added and the digestion continued for a few minutes on the steam bath. Much more water is then added and the undissolved silica is filtered, ignited, and weighed.
6. Finally the weight of the crude silica is corrected by adding about two drops of sulfuric acid together with 5 cc. of hydrofluoric acid and evaporating to dryness. After ignition the loss in weight is that of the silica.

There are differences of opinion as to the best method of procedure in each of the above mentioned steps[1], but the main point of difference seems to be over the fourth step in the above outline. Hillebrand[2] insists upon the necessity of at least two evaporations with hydrochloric acid and with intervening filtration; but finds no advantage in drying at temperatures above that of the steam bath.

The quantity of the residue(obtained in number 6), as well as its composition, seems to be a much disputed

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[1] U. S. Geol. Survey, Bull. 422, pp. 83-96.
[2] Jour. Am. Chem. Soc. Vol. 24, 1, 1902, p. 362.

point. Hillebrand[1] states that "the qualitative composition of this residue varies with the different rocks less than its quantity.....calcium is rarely if ever present, if the decomposition of the rock powder was complete at the outset.....the residue after its resolution is quantitatively precipitated by ammonia in the presence of an ammonium salt." Flynn[2], working with two samples of silicate rock,reported residues varying in weight from .0020 gm. to .0062 gm. These residues, according to Flynn, all contained calcium oxide in appreciable amounts.

A silicate rock is usually a very complicated substance with which to deal, the number of ingredients being often as high as twenty. A complete analysis, therefore, is difficult to accomplish; and when an attempt is made to study the effect of any one factor on the amount of the residue from the silica determination, many difficulties are encountered. It was to avoid these difficulties that the synthetic method was used. Accordingly a sodium carbonate fusion was made of a mixture containing only pure silica and lime; and therefore no unknown factors were introduced.

[1] U.S. Geol. Survey. Bull. 422, p. 83-96.
[2] Thesis, B. A., 1909, Wisconsin.

Reagents

Pure silica was prepared by treating an impure variety with hydrofluoric acid and passing the resulting silicon tetrafluoride gas into water. The silicic acid thus obtained was washed with dilute sulfuric acid, then with water until free from sulfates, and finally heated in five gram quantities over the blast for about two hours in platinum dishes. This silica gave no residue when evaporated with sulfuric and hydrofluoric acids. The sodium carbonate and precipitated calcium carbonate were free from magnesium and contained only a trace of iron. The sulfuric and hydrofluoric acids here employed gave no residues upon evaporating in platinum; and the hydrochloric acid[1] contained no trace of iron.

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1. The HCl used in Series I contained a trace of iron. A pure acid was used in all the remaining work.

Experimental

About .4 gm. of the silica was placed in a weighed platinum crucible and heated over the blast lamp until the weight was constant. This blasting required from 20 to 40 minutes. The loss in weight at times amounted to from .001 gm. to .003 gm, but when the state of complete dehydration was reached the silica was not hygroscopic. A weighed amount of calcium oxide was next added, then four parts of sodium carbonate to one of the mixture of silica and lime and the whole intimately mixed. Each analysis was carried out as previously outlined for a silicate rock, using two evaporations with intervening filtration, as suggested by Hillebrand[1] except that after the first evaporation, heating was continued in an air bath at 110 degrees for an hour. The results are given in Table I.

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1. U. S. Geol. Survey, Bull. 422, p. 91.

Table I.

No.[1]	gm. SiO_2	gm.[2] SiO_2	per cent[3]	gm. CaO used[4]	gm. residue[5]	gm. CaO in residue[6]	gm. $CaSO_4$ calculated[7]
1.	.3979	.3958	99.47	.10	.0014	.0006	.0015
2.	.3999	.3983	99.59	.21	.0023	.0005	.0012
3.	.3953	.3930	99.42	.20	.0018	.0006	.0015
4.	.4439	.4322	97.36	.40	.0014	.0006	.0015
5.	.3902	.3830	98.15	.60	.0016	.0006	.0015

1. Numbers 1, 2 and 4 were evaporated in platinum, and numbers 3 and 5 in porcelain.
2. Loss in weight when treated with hydrofluoric and sulfuric acids.
3. Per cent of silica recovered.
4. Weight of lime used in fusions.
5. Residue after evaporation of hydrofluoric acid.
6. Precipitated with ammonium oxalate and ignited.
7. CaO of residue calculated as $CaSO_4$ for comparison with residue which was weighed as sulfate.

The residues[1] were ignited to a constant weight over the blast. Each was then dissolved by digestion with concentrated hydrochloric acid. The solution was then diluted to about 100 cc, heated to boiling, made slightly alkaline with ammonia and the precipitate if any filtered out. Ammonium oxalate was then added to the boiling filtrate and the precipitated calcium oxalate allowed to settle; after which it was collected on a filter ignited and weighed as calcium oxide. From these results the calcium sulfate equivalent[2] was calculated for the sake of comparison with the original residue which was weighed as the sulfate.

Without a single exception these results prove the presence of calcium in the residue[3], and under these conditions it appears that the residue contains nothing but calcium sulfate. The percentage of lime in the fusion, however, has no effect upon the quantity to be found in the resulting residue. Number I, for example, in which .10 gm. of calcium oxide was used gave a residue of .0014 gm, while number 4, containing .40 gm. of calcium oxide gave the same amount of residue. The other results point

1. See note 5, Table I.
2. See note 7, Table I.
3. See note 5, Table I.

to the same conclusion. However, ammonium oxalate always gave a precipitate which was both visible and weighable, which showed that under the above conditions the residue was calcium sulfate.

The next thing attempted was a check on the two methods of dealing with the solution of the sodium carbonate fusion. Accordingly analyses were made using, in the one case, three evaporations with concentrated hydrochloric acid, (lettered A in Table II.) and, in the other, two evaporations with intervening filtration (lettered B in Table II). The fusions were made with a constant quantity (.10 gm.) of calcium oxide, about .4 gm. of silica and 2.4 gm. of sodium carbonate. Each analysis was continued as previously outlined and the drying completed by heating for an hour in an air bath at 110 degrees. For this purpose an asbestos lined oven, heated by two Bunsen burners, was used, and the temperature regulated by two thermometers.

Table II.

No.	SiO_2 used[1]	SiO_2 recovered[2]	Per cent[3]	Method[4]	Evaporated in
1.	.3893	.3845	98.79	A	porcelain
2.	.3911	.3869	98.93	B	" "
3.	.3922	.3858	98.37	A	platinum
4.	.3874	.3831	99.00	B	" "
5.	.3947	.3922	99.36	A	porcelain
6.	.3925	.3905	99.49	B	" "

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1. SiO_2 used in fusion.
2. Loss in weight on evaporation with hydrofluoric acid.
3. Per cent of SiO_2 recovered.
4. A-three evaporations.
   B-intervening filtration.

These results (Table II) seem to indicate that slightly more silica will pass into the filtrate after three evaporations with concentrated hydrochloric acid than after two evaporations with intervening filtration. There is not sufficient data, however, to justify any definite conclusion. But on the other hand, when the time required to make the analysis is considered, using three evaporations with but a single filtration has a decided advantage. It requires at least three hours to evaporate the extra water used in washing the second filtrate and this time is saved to the analyst by using the other method. The results shown in Table V were all obtained by the three evaporation method; and in all cases except one (No. 6, Table II) they show an improvement over the two filtration method in the percentage of silica recovered.

To account for the fact that silica always passed into the filtrate, several explanations have been offered. Hillebrand[1] claims that hydrochloric acid itself has a marked solvent action on silica. The above results appear to confirm this statement, for there is a loss on the average of about .004 gm. of silica which must have passed into the filtrate.

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[1] Jour. Am. Chem. Soc. Vol. 24, 1, p. 362.

In the course of a rock analysis some of this silica may be recovered with the precipitated iron and alumina. To test this point and to determine what amount of silica could be regained in this way, two analyses were made in which a small amount of ferric chloride was added to the filtrate after removing the precipitated silica, and the iron precipitated with ammonia. The ignited iron oxide was fused with potassium pyrosulfate, dissolved in dilute sulfuric acid, evaporated until fumes of sulfur trioxide were evolved, dissolved in water, filtered, and the silica corrected with sulfuric and hydrofluoric acids. The results are as follows:

Table III.

No.	gm. SiO_2 used	gm. SiO_2 recovered	gm. SiO_2 with iron	gm. SiO_2 total	per cent	T.
1.	.3896	.3859	.0030	.3889	99.82	120 deg.
2.	.3903	.3853	.0037	.3890	99.65	120 deg.

In Table III if will be noticed that after adding the weight of silica recovered with the iron there is still a loss of from .0007 gm. to .0013 gm.(or .2%-.3%).

One cause of this might be sought for in the pyrosulfate fusion. To test this point portions of silica weighing from .0097 gm. to .0198 gm. were fused with 6 gm. of potassium phrosulfate. The fusion was continued for one hour, then cooled, dissolved in dilute sulfuric acid, evaporated to fumes of sulfur trioxide, dissolved in water, and the silica filtered off, ignited, weighed, and corrected with sulfuric and hydrofluoric acids. The results are given in Table IV.

Table IV.

No.	gm. SiO_2 used	gm. SiO_2 recovered	gm. SiO_2 lost	gm. $K_2S_2O_7$
1.	.0198	.0189	.0009	6
2.	.0097	.0088	.0009	6
3.	.0197	.0189	.0008	6
4.	.0110	.0101	.0009	6

The results show a loss of .0009 gm. of silica which was probably dissolved by the pyrosulfate; hence it appears that even this treatment will not regain all of the silica which first passed into the filtrate.

Since, as has been demonstrated, the hydrochloric acid has a solvent action upon silica, it follows that the concentration of this acid and also the amount of water used in washing the filtered silica would be factors in determining the amount that would be dissolved. Now the amount of acid used was kept as near constant as possible; but the quantity of water used in washing the silica naturally varied to some extent. In all cases this washing was carried on until a few drops of the filtrate gave no test for chlorides when treated with silver nitrate. In the first series (Table I) no more water was used than was necessary to reach this point; but in Series V, the washing was continued still further, using in all about 400 cc. of water. The results show the effect; for the residues obtained in the first series are larger than those obtained when using this excessive amount of water in washing. Moreover the percent of silica found is more consistent in the latter case.

In order to determine the effect produced by using different drying temperatures, a series of analyses was made, keeping the other factors as nearly constant as possible, but varying the temperature. First steam

bath temperature was used, then 120 degrees, and finally 200 degrees. Four determinations of the silica and the residue were made at each of these temperatures, using the method as previously outlined. A constant quantity of lime (about .10 gm.) weighed as calcium carbonate was used in all cases, and fusion was made with about .4 gm. of silica and 2 gm. of sodium carbonate. The results are given in Table V.

Table V[4]

T.[1]	No.	gm.[2] SiO_2 used	gm. SiO_2 recover	per cent SiO_2 recover	gm.[3] residue
100 deg.	1.	.3765	.3736	99.22	.0004
	2.	.4018	.3997	99.49	.0005
	3.	.4006	.3971	99.13	.0017[5]
	4.	.4073	.4044	99.28	.0005
120 deg.	1.	.3903	.3873	99.22	.0006
	2.	.4063	.4032	99.24	.0006
	3.	.4166	.4142	99.42	.0005
	4.	.4003	.3978	99.38	.0005
200 deg.	1.	.3983	.3951	99.19	.0012
	2.	.3973	.3949	99.40	.0010
	3.	.3998	.3975	99.40	.0010
	4.	.3989	.3953	99.08	.0013

1. Drying temperature.
2. SiO_2 used in fusion.
3. Residue after treatment with hydrofluoric acid.
4. Three evaporations with concentrated HCl.
5. Contained iron, probably dust from hood.

A common explanation of the fact that silica always passes into the filtrate is the theory that a soluble silicate is re-formed by the heat applied during the dehydration process. If this is true an increase in the drying temperature should give a corresponding decrease in the amount of silica regained. The results in Table V show only a very slight tendency in this direction. By continuing the results obtained at 100 degrees, 120 degrees and 200 degrees, respectively, we get the following average per cents:

100 degrees	99.28
120 degrees	99.32
200 degrees	99.27

These figures indicate that the temperature of dehydration has only a slight effect upon the silica determination under the conditions used here; but if iron had been present this high drying temperature - 200 degrees - would have caused a certain volatization of the chlorides. Even under these conditions the extremely high temperature recommended by Bertram Blont[1] did not increase the per cent of silica recovered; but on the

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[1] Jour. Am. Chem. Soc. Vol. 21, 1902, p. 217.

contrary gave lower results than were obtained by drying at even steam bath temperature. A stronger objection to this high drying temperature is shown by a glance at the residues obtained in Table V. This shows very plainly that the filtered silica was contaminated by an impurity, for the residues obtained at 200 degrees are, on the average, twice as great as those found at 120 degrees.

These residues obtained in this series (Table V) were dissolved in hydrochloric acid, and the first eleven combined and analyzed with the following results:

Sum of 11 residues	.0085
Fe_2O_3	.0014
CaO .... .0021 ... as $CaSO_4$	.0051
Correction for 11 filter papers	.0019
TOTAL	.0084

Practically all of the .0014 gm. of iron oxide in the above table may have come from No. 3. of the 100 degrees temperature series; since that residue is .0012 gm. larger than the others of the same series, and it was known to contain iron. The filter papers used give .00017 gm. ash each, and since this was left

in the residue, the correction was made as indicated. The results, therefore, tend to prove that under these conditions the residue is almost entirely calcium sulfate.

Discussion.

After treating the silicate fusion as previously outlined the silica always leaves a residue which can be quantitatively precipitated as calcium oxide. There can be no doubt, therefore, that calcium is an essential constituent of this residue. This does not agree with the statement made by Hillebrand[1] that "the residue is quantitatively precipitated by ammonia in the presence of an ammonium salt". It does, however, agree with the work done by Flynn[2], who worked with silicate rocks and in all cases found calcium in these residues.

This fact that lime always sticks with the silica so that it is beyond the power of hydrochloric acid and water to completely remove it, points to the formation of a chemical compound. No change in the residue was noticed, however, when the proportion of lime to silica

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1. U. S. Geol., Survey, Bull. 422, p 97.
2. Thesis B. A., 1909, Wisconsin.

was varied. But the fact that increasing the drying temperature of the hydrochloric acid solution of the fused mass did increase the amount of the residue, tends to show that a silicate of calcium was formed. Reference to Table V will show that heating to 200 degrees had the effect of doubling the amount of the residue. This indicates that a compound of lime and silica was formed, this compound being again decomposed by the subsequent treatment with hydrofluoric acid in volatilizing the silica.

With regard to the drying temperature to be used in a regular silicate analysis, even 120 degrees might cause some of the chlorides to volatilize. The usual dehydration temperatures of 105 degrees to 108 degrees would be practically as effective as higher temperatures; since, judging from the results obtained[1] there is little choice between steam bath temperature and 120 degrees. Practically the same amount of silica is lost in each case.

The fact that silica always passes into the filtrate brings up the question as to whether a factor might not be introduced to correct for this error. It is the

[1] Table V.

practice of some chemists to attempt to recover this silica from the precipitated iron and alumina; but that more or less escapes even this treatment is evident when the fact that pyrosulfate[1] itself dissolves a certain amount of silica is considered. Hillebrand[2] states that .0058 gm. to .0060 gm. of silica was dissolved in a pyrosulfate fusion. But he failed to give the quantities of silica and pyrosulfate used in making these fusions. The results obtained in this work are lower probably because less pyrosulfate was used. Hillebrand[2] also gives data to show that silica is dissolved by hydrochloric acid. His results show that from .0022 gm. to .0029 gm. passed into the filtrate when silica was digested with hydrochloric acid, (S.G.1.1.). Our results agree very well with this as may be seen from Table V. The greatest loss there shown is .0036 gm. and the smallest .0021 gm. Since a certain amount of silica always passes into the filtrate; and since it is practically impossible to recover all of this by any subsequent treatment; it appears that it might be better to apply a solubility factor and thus get a closer approximation to the true amount of silica present

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[1] Table IV.
[2] Jour. Am. Chem. Soc. Vol. 24, 1, p. 362.

than could be obtained by any other means. Consider Table V for example; if for each .4000 gm. silica .0028 gm. is added to each of the weights of silica regained, no result will vary from 100% by more than .22%; and the average of any of the series of four results taken at the different temperatures will in no case vary more than .03% from the 100% value. This is clearly as near the true result as anyone could get by adding the fraction of silica which might be regained later with the iron and alumina in the course of an analysis. The effect of applying this factor is shown by recalculating Table V. When .0028 gm. is added to the silica actually recovered the results appear as given in Table VI.

Table VI.

T.	No.	Gm. SiO_2 used	Gm. SiO_2 recovered	Per cent by experiment	Per cent corrected
100 deg.	1.	.3765	.3764	99.22	99.92
	2.	.4018	.4025	99.49	100.19
	3.	.4006	.3999	99.13	99.83
	4.	.4073	.4072	99.28	99.98
120 deg.	1.	.3903	.3891	99.22	99.92
	2.	.4063	.4060	99.24	99.94
	3.	.4166	.4170	99.42	100.12
	4.	.4003	.4006	99.38	100.08
200 deg.	1.	.3983	.3979	99.19	99.89
	2.	.3973	.3977	99.40	100.10
	3.	.3998	.4003	99.40	100.10
	4.	.3989	.3981	99.08	99.78

General Conclusions.

1. Calcium is a usual constituent of the residue and can be recovered later by ammonium oxalate precipitation.

2. The proportion of the lime used in the fusion does not affect the amount of the residue.

3. The method of three evaporations with hydrochloric acid (S.G.1.2.) appears to give as good results as can be obtained by two filtrations, and with a large saving of time.

4. The temperature used in drying should not exceed 120 degrees. Higher temperatures are dangerous as they increase the residue and may re-form soluble silicates.

5. Silica is dissolved by the hydrochloric acid extraction. Not all of this dissolved silica can be recovered later.

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BY Victor Lenher

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